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(54) Particulate Al alloy composites.

(57) A particulate composite having a continuous phase of a metal such as an Al alloy and a disperse phase, incorporated in the continuous phase, of a refractory material such as SiC. The composite is made by atomising a stream (12) of the Al alloy to form a spray (22) of metal droplets, and applying fine refractory material (24) to the stream or spray. The resulting particulate composite may be consolidated to produce solid products.

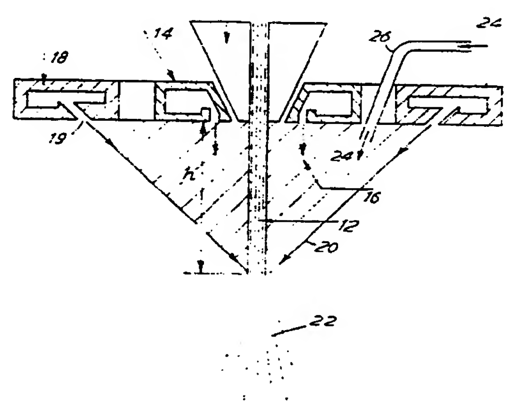

FIG. 1

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PARTICULATE METAL COMPOSITES

This invention relat s to particulate composites in which the particles have a continuous phase of a metal eg an Al alloy.

EPA 105595 describes Al alloys containing substantial proportions of Cr, Zr and Mn. Rapid cooling of the molten alloy e.g. by spraying or splatcasting, results in a particulate solid in which the bulk of the alloying additions are retained in solid solution. This material can be consolidated by powder metallurgy techniques to a product which can be age-hardened at a temperature of 300° to 500° and which retains its strength for long periods at temperatures of 150°C to 450°C.

EPA 128260 describes a technique employing metal vapour to make composite particles below 10 microns.

GB 2115014 describes a method of making a massive (i.e. not particulate) product by combining molten metal droplets with fine refractory material.

DE 2124199 describes an atomisation method of making metal powders whose particle surfaces are coated with fine refractory material.

EPA 147769 describes a method of making particulate composites of Al alloys with fine refractory material, by mechanical alloying.

GB 1548616 is one of a family of patents relating to the manufacture of spray deposited preforms from which articles of precise shape can be produced e.g. by forging, pressing or machining. A stream of molten metal alloy is atomised by means of high velocity jets of gas and the resultant spray of hot metal particles is directed onto a shaped collecting surface to form a coherent deposit. The patent describes how a proportion of the particles may miss the target and collect as a powder or aggregate of overspray material which is not convenient for re-cycling and, it is implied, not useful for other purposes.

EPA 198607 describes a method of making a metal matrix composite comprising the steps of atomising a stream of molten metal to form a spray of hot metal particles by subjecting the stream to relatively cold gas directed at the stream, applying to the stream or spray fine solid particles of a material of different composition from the metal, and depositing the metal, having said fine particles incorporated therein, in coherent form on a collecting surface. The fine particulate material enhances physical and mechanical properties of the metal matrix. The metal may be Al and the particulate material may be SiC.

When the method of EPA 198607 is operated, a proportion of the metal particles is generally not deposited on the collecting surface, and is collected downstream as a powder or aggregate. The present invention is based on the following observation regarding the overspray. When a finely divided refractory material has been applied to the stream or spray of molten metal, the refractory material is found, not only in the coherent deposit formed on the collecting surface, but also associated with the metal in the overspray. The refractory material is present in the overspray, not only on the surface of the solidified particles of metal, but also rather uniformly distributed within the interior of the particles. This observation was unexpected. It had not previously been realized that the refractory material became associated with the molten metal spray prior to deposition on a collecting surface. Indeed, the prior art noted above indicates that such association would not take place.

The present invention provides a particulate composite, made by combining molten metal droplets with fine refractory material, in which the particles have a continuous phase of the metal and a disperse phase, incorporated in the continuous phase, of the refractory material.

The invention is of particular interest when the metal is an Al alloy, as the technique of atomising molten Al alloys is quite well developed. But the invention is applicable to other materials that can be sprayed in the form of molten droplets, such as for example, steel, nickel, cobalt, copper, titanium and magnesium.

The particulate composite has been made by combining molten metal droplets with fine refractory material. Even when spray casting is carried out in an inert atmosphere, so far as Al allows are concerned, the resulting particles necessarily have at least a thin oxide coating on their surface. The particles do not normally contain any internal oxide inclusions unless this is deliberately added in (or as) the fine refractory material. By contrast, a particulate composite of an Al alloy made by mechanical alloying would necessarily contain internal oxide inclusions.

The particles of the composite generally hav a size in the range from 10 to 500 microns, preferably with an average diameter of from 20 to 80 microns. When the particles are formed by spray casting, their diameter can be controlled by controlling the atomising conditions, as is known in the art. Although they may be flattened, e.g. as a result of splat-casting, the composite particles are preferably spherical.

The refractory material may be another metal of high melting point than the metal, but is preferably an oxide, boride, carbide or nitride. Ceramic materials of this kind, some of which are known as refractory hard metals, are well known, and preferred examples include SiC, A1 O , MgO, TiC and boron carbide. These refractory materials are preferably used in the form of particles having average diameters, below 50 microns and down to sub-micron size. Particles of 5 to 20 microns are often convenient to use.

In the composite particles, the disperse phase and the continuous phase are preferably present in volume concentrations of 0.5 to 50% and 99.5 to 50% respectively. Particularly when used in a volume concentration of 10 to 30%, high strength high modulus refractory powders can impart substantial strengthening and modulus properties to the composite.

The matrix metal may be an Al alloy containing on or more conventional age-and solution-hardening ingredients such as Zn, Mg, An, Si, Li, and optionally also one or more transition metal elements for grain refining purposes.

Or the Al alloy may contain at least one transition metal alloying ingredient having age-hardening, or solution strengthening properties, such as for example Cr, Zr, Mn, Fe, Co and Ce. Preferred are alloys containing 0.5% to 7% by weight Cr, 0.5% to 2.5% by weight Zr and 0.1% to 4.0% by weight Mn. These alloying ingredients are difficult to get into solid solution in Al by conventional means, but this problem is solved by the spray-casting technique described below. These transition metal alloying elements have the advantage of providing age-hardening properties at elevated temperatures typically in the range 300°C-500°C.

The transition metal alloying ingredients are preferably present at least partly, and preferably totally, in solid (supersaturated) solution in the metal. When not in solid solution, the alloying ingredients should be present as a fine dispersion. To achieve this, it is necessary to cool the molten metal rapidly at about 10°C sec for a fine dispersion, and at about 10°C sec for solid solution. Depending on particle size, these are cooling rates which can be achieved by spray-casting.

In another aspect, the invention provides a method of making the particulate composite herein described, which method comprises atomising a stream of the molten metal to form a spray metal particles by subjecting the stream to relatively cold inert gas directed at the stream, applying to the stream or spray fine solid particles of a refractory material, allowing the metal particles to solidify, and collecting the resulting particulate composite.

Preferably, the solid particles of refractory material are applied to the stream of molten metal just before this is broken up into spray. In order to obtain spherical particles it is, of course, necessary that the metal particles solidify before impact with any solid surface. For Al alloys the inert gas may conveniently be argon or preferably nitrogen. Providing the oxygen partial pressure is sufficiently low, the composite particles come out spherical with no more than a thin coating of aluminium oxide. The spray of molten metal particles may be directed at a collecting surface, in which case a particulate composite is recovered as a by-product. Alternatively, the spray conditions may be chosen such that the metal particles solidify before impact with any solid surface.

The nature of the Al alloy is not critical to the invention. The method has been employed to make particulate composites using SiC as the refractory material with the following: commercially pure aluminium, AA 2014, 2024, 2618, 6061, 7075, 7475, 8090, LM 13, A 3210, Al-12% Si, Al-20% Si and Al-6% Sn.

The particulate composite is amenable to further processing via known powder metallurgy routes such as canning, degassing, compacting and extruding to solid eg semi-fabricated or fully fabricated products. Possible applications include extruding directly to form air-frame structures; extruding bar and forging to give gas-turbine compressor blades or pistons for internal combustion engines; or extruding plate and rolling to sheet for the skins of aircraft.

Reference is directed to accompanying drawing which is a diagram of an atomisation system suitable for making particulate composites of the invention. The system comprises a molten metal nozzle 10 from which is passing by gravity a stream 12 of molten metal. Surrounding the molten metal nozzle is a primary gas nozzle 14, with apertures to direct a primary support gas flow 15, parallel to and surrounding the metal stream, to shroud and contain the molten metal. Surrounding the primary gas nozzle is a secondary gas nozzle 18 provided with jets 19 which direct a secondary atomising gas stream 20 towards the molten metal stream. The secondary gas stream contacts the molten metal stream a distance h downstream of the molten metal nozzle and atomises it into a spray 22 of metal particles.

The secondary atomising gas flow 20 d fines a cone of height h and radius equal to the distance of the jets 19 from the metal stream 12. The refractory material 24, entrained in a carrier gas, is introduced into this cone via a pipe 26. The carrier gas flow rate is typically several orders of magnitude less than th flow rate of the secondary atomising gas 20.

The position at which the carrier material is introduced within the cone is not critical; it could for example be inside, rather than outside, the primary gas nozzle 14. If the distance h is sufficiently small, it is possible to dispense with the primary gas nozzle altogether.

The refractory material loading in the carrier gas, and the carrier gas flow rate relative to the metal flow rate and the secondary (atomising) gas flow rate determine the concentrations of refractory material in the particulate composite produced. The temperature and flow rate of the atomising gas determine the rate at which the atomised metal particles solidify.

The following examples illustrate the invention.

Example 1

A typical experiment resulting in the formation of composite powder (18% of 13 microns SiC powder into AA 2014 alloy) was carried out using the following parameters in a system as shown in the figure:-

(a) Temp. of molten metal = 705°C

(b) Primary gas - pressure = 0.25 MPa - flow rate = $0.4 m^3 min^{-1}$ -approx velocity = 240 $m\ sec^{-1}$

(c) Secondary gas - pressure = 0.55 MPa - flow rate = 6.0 $m^3 min^{-1}$ -approx velocity = 300 $m\ sec^{-1}$

(d) Carrier gas SiC loading = 30 $kg\ m^{-3}$

(e) Carrier gas flow rates = 0.03 $m^3 min^{-1}$

The product collected consisted of some SiC that did not get incorporated, along with the desired product, which was characterised as follows:-

(a) Composite powder size range = 10-500 microns

(b) Mean size of composite = 80 microns

(c) SiC size range in composite = 6-45 microns

(d) Mean size of SiC in composite = 13 microns

(e) Vol % SiC in the composite powder = 18%

The SiC and Al-SiC composite powders can be separated either by sieving or by gas separation/classification techniques. An optical section through the composite particles shows comminuted SiC uniformly distributed through the metal matrix.

Example 2

The amount of SiC (or other refractory material) incorporated is dependent on the composition of the Al alloy used and on the atomising conditions. The following table reports the % SiC incorporated in a series of experimental runs performed under the same general conditions as Example 1. The % SiC was determined by sieving the particulate composite to -150 to +38 microns (thereby excluding SiC particles not associated with Al metal), followed by chemical dissolution of the matrix and weighing.

SiC Secondary Atomising Pressure
and Mean Diameter

Alloy	Weight % SiC	Volume % SiC	Secondary Pressure	Composite Mean Diam
2014	21.3	18.6	8.0	67.4
6061	28.4	24.8	8.0	68.6
2014	14.5	12.6	7.0	68.8
2014	12.0	10.5	5.3	78.0
2014	17.3	15.1	6.3	70.8
8090	5.5	4.4	5.8	69.2
2014	12.2	10.6	4.7	71.5

Example 3

Two experiments have been conducted both using 2014 alloy and the same powder production conditions as in Example 1. They differ in their processing after the powder production phase.

Experiment A

The as produced powder was sieved to <150µm and then air classified to >45µm producing a composite powder in the size range 45-150µm. The powder was placed in a can (170 mm diameter by 647 mm length) made of 6082 alloy and degassed at 325 C for 4 hours under vacuum. The can and powder were then hot compacted at 350°C in a commercial press. After cooling the can was machined away.

The hot compacted billet was extruded using an indirect press to a rectangular section 63 mm x 14 mm corresponding to an extrusion ratio of 26:1.

The as-extruded bar was solution heat treated for 1 hr at 505°C, water quenched, and artificially aged for 8 hr at 175°C. Tensile test data was obtained using round bar tensiles machined parallel to the extrusion direction.

Experiment B

The as-produced powder was sieved to <150 m and then air classified to >25 m producing a composite powder in the size range 25-150 m. The powder was placed in a can (74 mm diameter by 200 mm length) made of 2024 alloy. Two degassing conditions were used; 4 hrs at 325°C and 1 hr at 530°C under vacuum. The cans were sealed and then put into a furnace at 300°C fo 30

Property	Experiment A	Experiment B Degassing Temperature 325°C	530°C	2014
0.2% PS (MPa)	430	414.2	442.4	429
TS (MPa)	474	462.7	491.7	476
Ef (%)	3.7	2.3	1.5	7.5
E (GPa)	87	96.0	90.4	73

PS - proof strength
TS - tensile strength
Ef - elongation to failure
E - elastic modulus

Claims

1. A particulate composite, made by combining molten metal droplets with fine refractory material, in which the particles have a continuous phase of the metal and a disperse phase, incorporated in the continuous phase, of the refractory material.

2. A particulate composite as clained in claim 1, wherein the metal is an Al alloy.

3. A particulate composite as claimed in claim 2, wherein the Al alloy includes at least one transition metal element at least partly in solid solution.

4. A particulate composite as claimed in any one of claims 1 to 3, wherein the particles are spherical.

5. A particulate composite as claimed in any one of claims 1 to 4, wherein the refractory material is an oxide, boride, carbide or nitride.

6. A particulate composite as claimed in any one of claims 1 to 4, wherein the particles have a size in the range 10-500 microns.

7. A particulate composite as claimed in any one of claims 1 to 6, wherein the refractory material is in the form of particles having an average diameter of up to 50 microns.

8. A particulate composite as claimed in any one of claims 1 to 7, wherein the refractory material is uniformly distributed within the particles.

9. A particulate composite as claimed in any one of claims 1 to 8, wherein the continuous phase is of an Al alloy containing a transition element selected from 0.5% to 7.0% by weight Cr, 0.5% to 2.5% by weight Zr , and 0.1% to 4.0% by weight Mn.

10. A method of making the particulate composite claimed in any one of claims 1 to 9, which method comprises atomising a stream of a molten metal to form a spray of metal particles by subjecting the stream to relatively cold inert gas dir cted at the stream, applying to the stream or spray fin solid particles of a refractory material, allowing the metal particles to solidify, and collecting the resulting particulate composite.

11. A method as claimed in claim 10, wherein the solid particles of refractory material are applied to the stream of molten metal.

12. A solid body formed by compacting the particulate composite of any one of claims 1 to 9.

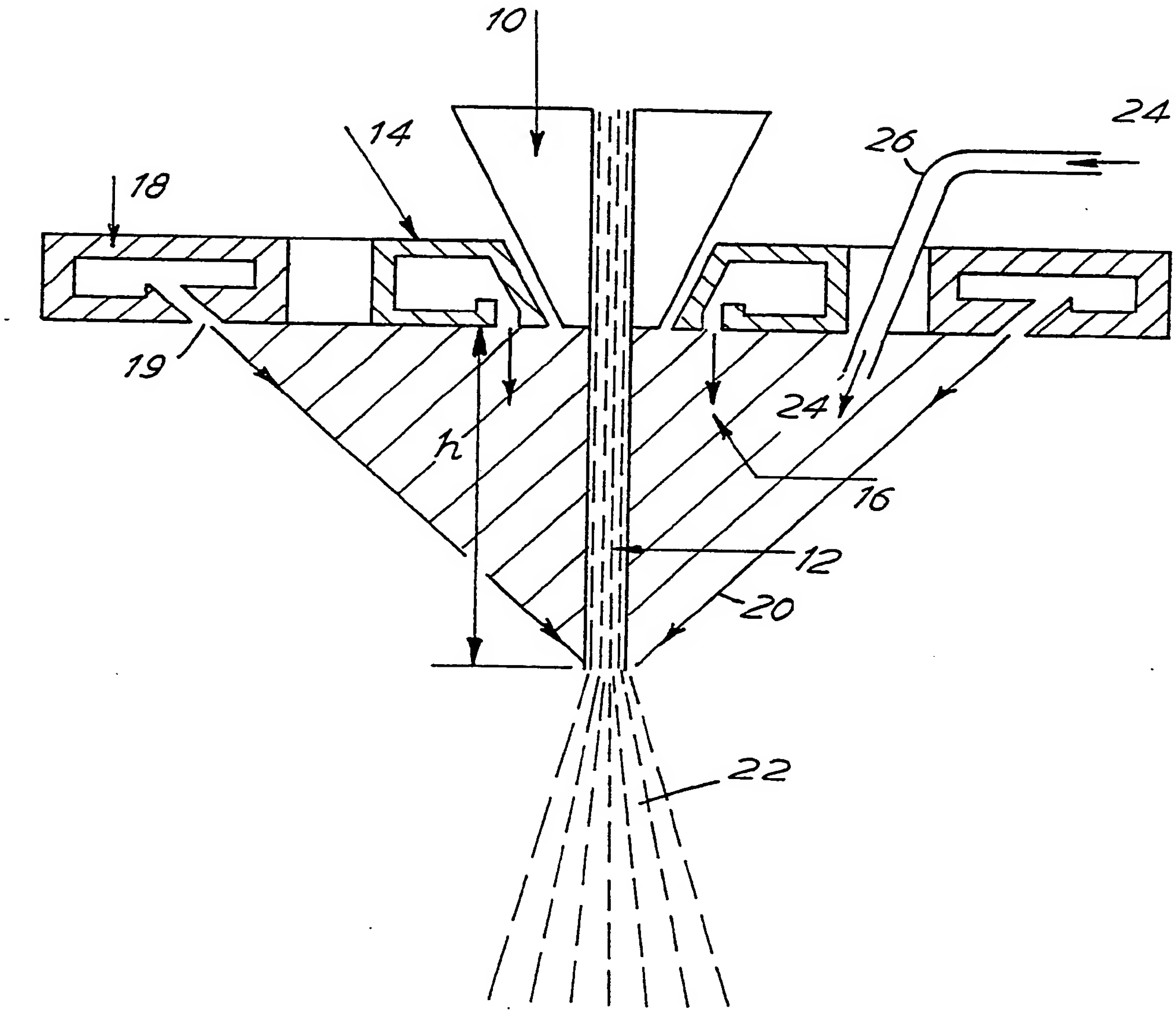

FIG. 1

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EUROPEAN SEARCH REPORT

Application Number

EP 87 30 8466

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X Y	DE-A-3 428 022 (H.C. STARCK) * Whole document *	1,4,5,8,10-12 2,3,6,7,9	C 22 C 1/10 C 22 C 32/00 B 22 F 9/08
Y,D	EP-A-0 128 360 (TOYOTA) * Claims 1-8,12-14 *	2,3,6,7,9	
X,D	EP-A-0 147 769 (SUMITOMO) * Claims 1,2,4; abstract *	1-9,12	
E	EP-A-0 225 080 (OSPREY) * Claims 13,15 *	10,11	
X	GB-A-2 146 662 (TELEDYNE IND.) * Claims 1,6-9; page 4, lines 5,11 *	10,11	
X,D	DE-B-2 124 199 (MANNESMANN) * Claim 1; column 2, line 68 - column 3, line 5 *	10,11	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A,D	GB-A-2 115 014 (NATIONAL RESEARCH DEVELOPMENT CORP.) * Claims 1,7,10-14 *	10,11	C 22 C B 22 F B 22 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15-12-1987	SCHRUERS H.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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